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1. Title of the invention

Terminal reactive polymer

2. Scope of the Claim for Patent

(1) A silane or siloxane-modified polymer containing a hydrolyzable functional group at a polymer terminal end obtained by reacting a living polymer obtained by polymerizing monomer in an inert solvent using an alkali metal or an organic alkali metal catalyst with at least one molecule of a silane or siloxane compound having at least two hydrolysable functional groups in one molecule per one active terminal end of the living polymer.

(2) A polymer according to claim 1, wherein the monomer is at least one of monomers of conjugated dienes and vinyl aromatic hydrocarbons.

(3) A polymer according to claim 1 or 2, wherein the living polymer is a block copolymer having at least one polymer block mainly comprising a conjugated diene and having at least one

polymer block mainly comprising a vinyl aromatic hydrocarbon.

(4) A polymer according to claim 1 and 3, wherein the silane compound having at least two hydrolysable functional groups in one molecule is represented by the general formula (I):



(wherein X represents a halogen atom, Y represents a hydrolysable organic group other than the halogen, R represents an alkyl group, aryl group, vinyl group, or halogenated alkyl group, n is 0 or 1, m is an integer of 1 to 4, providing that the sum for n + m is at least 2 or greater).

(5) A polymer according to any one of claims 1 to 4, wherein the hydrolysable functional group at the terminal end of the silane or siloxane modified polymer is an alkoxy group bonded directly to a silicon atom.

(6) A polymer composition that can be high-polymerized or crosslinked in contact with water, containing a silane or siloxane modified polymer containing a hydrolysable functional group at the polymer terminal end, and a silanol condensation catalyst, by reacting a living polymer obtained by polymerizing monomer in an inert solvent using an alkali metal or an organic alkali metal catalyst with at least one molecule of a silane or siloxane compound having at least two hydrolysable functional groups in one molecule per one active terminal end of the living polymer.

(7) A polymer composition according to claim 6, wherein the

monomer is at least one of monomers of conjugated dienes and vinyl aromatic hydrocarbons.

(8) A polymer composition according to claim 6 or 7, wherein the living polymer is a block copolymer having at least one polymer block mainly comprising a conjugated diene and having at least one polymer block mainly comprising a vinyl aromatic hydrocarbon.

(9) A polymer composition according to claim 6 or 8, wherein the silane compound having at least two hydrolysable functional groups in one molecule is represented by the general formula (I).



(where X represents a halogen atom, Y represents a hydrolysable organic group other than the halogen, R represents an alkyl group, aryl group, vinyl group, or halogenated alkyl group, n is 0 or 1, m is an integer of 1 to 4, providing that the sum for n + m is at least 2 or greater).

(10) A polymer composition according to any one of claims 6 to 9, wherein the hydrolysable functional group at the terminal end of the silane or siloxane modified polymer is an alkoxy group bonded directly to a silicon atom.

3. Detailed Description of the Invention

The present invention is related to a polymer having a hydrolyzable silane or siloxane group at a terminal end

obtained by reacting a living polymer and a silane or siloxane compound having two or more functional groups, and a polymer composition that can be high-polymerized or crosslinked in contact with water comprising the polymer and a silanol condensation catalyst.

Conjugated diene polymers, vinyl aromatic hydrocarbon polymers, and conjugated diene-vinyl aromatic hydrocarbon copolymers obtained by polymerizing a conjugated diene or a vinyl aromatic hydrocarbon in an inert solvent by using an alkali metal or an organic alkali metal catalyst are used in a wide range as synthesis rubbers or synthesis resins.

Generally, physical properties of the polymers described above can be improved by increasing the molecular weight. However, production of high molecular weight polymers by solution polymerization increases the solution viscosity extremely highly making it difficult for stirring, transportation, and drying of a polymer solution to require enormous energy, as well as requires special facilities and, particularly, in a case where the polymerization degree is high, production is impossible. Further, in living polymerization of using an alkali metal catalyst or an organic alkali metal catalyst, since the molecular weight is in proportion to the reciprocal of the catalyst amount, the catalyst amount has to be decreased in a reverse proportional manner for producing a polymer of high molecular weight, which makes the control

of the molecular weight extremely difficult. This is because, in a case where the amount of the catalyst is small, the effective amount of the catalyst used for the polymerization undergoes a remarkable effects when the extent of the impurities in the solvent or the monomer or the stains of the reactor that deactivate the catalyst is changed.

Further, the block copolymer of the conjugated diene and the vinyl aromatic hydrocarbon is used as a thermoplastic elastomer when it mainly comprises the conjugated diene and as a transparent impact resistant resin when it mainly comprises the vinyl aromatic hydrocarbon. In any of the cases, since the copolymer has the vinyl aromatic hydrocarbon polymer block, it shows thermoplasticity and can be molded by injection molding, extrusion molding, blow molding, compression molding, etc. as a usual fabrication method. However, in the polymers described above, the molecular weight is generally restricted low for maintaining excellent fabricability and their physical properties are not always favorable. Particularly, in a case of the thermoplastic elastomer, since this is a linear polymer different from crosslinked rubber, physical properties, for example, strength, rigidity, heat resistance and oil resistance are poor.

As described above, while the polymer of low molecular weight is easy to be produced and excellent in the fabricability, it is poor in the physical property. On the other hand, while

a polymer of high molecular weight is excellent in the physical property, production is difficult or impossible and, in addition, the fabricability is poor.

The present inventors have made an earnest study for overcoming the foregoing problems and have accomplished the present invention based on the concept and the finding quite different from those in the prior art.

That is, the invention provides a silane or siloxane modified polymer (hereinafter referred to as "silane-modified polymer") containing a hydrolyzable functional group at a polymer terminal end obtained by reacting a living polymer obtained by polymerizing monomer in an inert solvent using an alkali metal or an organic alkali metal catalyst with at least one molecule of a silane or siloxane compound having at least two hydrolysable functional groups in one molecule per one active terminal end of the living polymer and, further, a polymer composition that can be high-polymerized or crosslinked in contact with water, containing the silane-modified polymer and the silanol condensation catalyst.

Since the silane-modified polymer of the invention is a polymer having a usual molecular weight, it can be synthesized easily by a usual production process and can also be molded easily. In addition, the silane-modified polymer can be high-polymerized or crosslinked optionally in admixture with

a silanol condensation catalyst and in contact with water, and the physical properties of the obtained high molecular weight polymer and the crosslinked polymer are outstandingly excellent over those before reaction.

The contents of the invention are to be described specifically.

The alkali metal or the organic alkali metal catalyst used in the invention includes, for example, lithium, sodium, cesium, n-butyl lithium, sec-butyl lithium, phenyl lithium, styrene dilithium, diisopropenyl benzene dilithium, sodium naphthalene and lithium naphthalene.

As the inert solvent used for the production of the living polymer and the reaction thereof with silane or siloxane compounds of the invention, hydrocarbon solvents such as pentane, hexane, cyclohexane, heptane, benzene, and toluene, and ether solvents such as tetrahydrofuran and diethyl ether are used. Further, it is also possible to add a polar compound in the solvent to increase the polymerization rate, change the copolymerization reactivity between the conjugated diolefin and the vinyl aromatic hydrocarbon, or change the micro structure. The polar compounds includes, for example, diglyme, triethylamine, diethylether, and tetrahydrofuran.

The monomer used in the invention includes all known monomers that conduct living polymerization by the alkali metal or organic alkali metal catalyst described above, and includes,

for example, conjugated diene, vinyl aromatic hydrocarbon, vinyl pyridine, methyl methacrylate, acrylonitrile, methylethacrylonitrile, and acrylate ester. They are preferably conjugated diene and vinyl aromatic hydrocarbons, including, for example, butadiene, isoprene, styrene, and α -methylstyrene.

For the method of polymerization of the living polymer used in the invention, any method known so far can be adopted. Generally, the inert solvent, the monomer, and the catalyst of the invention are charged in a reactor where the atmosphere for the polymerization system is replaced with a nitrogen gas and reaction is initiated. In this case, production can be conducted at a polymerization temperature within a range from -120°C to 150°C and, preferably, from -80°C to 120°C , at a concentration of the monomer in the solvent of usually from 5 to 50% and, preferably, from 10 to 35% and for a polymerization time within 48 hour, and preferably, from 0.5 to 10 hours. Optionally, the catalyst and the monomer may be supplementally added after starting the polymerization. The reaction may be conducted batchwise or continuously and includes any other method.

Further, for producing the living polymer, it is desirable to avoid deactivation of the catalyst and the living polymer as much as possible and, accordingly, it is necessary to take care so as not to intrude impurities, water, oxygen,

gaseous carbon dioxide or halogenation products having a deactivation effect into the polymerization system.

The living polymer of the invention is, preferably, living polymers of conjugated diene polymers, vinyl aromatic hydrocarbon polymers, and conjugated diene-vinyl aromatic hydrocarbon copolymers and, particularly preferably, block copolymers containing a polymer block mainly comprising at least one conjugated diene and a polymer block mainly comprising at least one vinyl aromatic hydrocarbon. The polymer block mainly comprising the conjugated diene may also contain a small amount of the vinyl aromatic hydrocarbon, or the polymer block mainly comprising the vinyl aromatic hydrocarbon may also contain the conjugated diene. The block copolymer includes complete, tapered, linear, branched, radial, and star-like block copolymers.

Usually, the conjugated diene polymer rubber or the conjugated diene-vinyl aromatic hydrocarbon copolymer rubber is used being vulcanized with sulfur or peroxide. On the other hand, the block copolymer is used not being crosslinked as a thermoplastic elastomer or a thermoplastic resin which is transparent and of good impact resistance. Accordingly, the effect of the invention is most conspicuous when applied to the block copolymer described above.

The functional group-containing silane and siloxane compound to be reacted with the living polymer of the invention

is a silane or siloxane compound containing at least two hydrolysable functional groups in one molecule and, preferably, a silane compound represented by the following general formula (I).



(where X represents a halogen atom, Y represents a hydrolysable organic group other than the halogen, R represents an alkyl group, aryl group, vinyl group or halogenated alkyl group, n is 0 or 1, m is an integer of 1 to 4, providing that the sum for n + m is at least 2 or greater).

The halogen atom includes chlorine, bromine, iodine, etc. and chlorine is preferred. Hydrolyzable organic groups other than the halogen atom include any hydrolysable organic group, for example, alkoxy groups such as methoxy group, and ethoxy group, acyloxy group such as formyloxy group, acetoxy group or propionyloxy group, oxime group, for example, $-\text{ON}=\text{C}(\text{CH}_3)_2$, $-\text{ON}=\text{OCH}_2\text{C}_2\text{H}_5$ and $-\text{ON}=\text{C}(\text{C}_2\text{H}_5)_2$, or substituted amino group, for example, alkylamino group and arylamino group, $-\text{NHCH}_3$, $-\text{NHC}_2\text{H}_5$, and $-\text{NH}(\text{C}_6\text{H}_5)$ and, preferably, the alkoxy group. The most suitable silane compound includes tetraethoxysilane, triethoxymonochlorosilane, diethoxy monochloromonomethylsilane, triethoxy monomethylsilane, trimethoxy monomethylsilane, diethoxy dimethylsilane, dimethoxy dimethylsilane, dimethyl diacetoxysilane, methyltriacetoxysilane, chloromethyl triethoxysilane, and

3-chloropropyl triethoxysilane.

The silane and the siloxane compounds can be used optionally each alone or as a mixture of two or more of them.

The number (n) for the halogen atoms in the general formula (I) is restricted to 1 or less. Usually, the Si-Cl bond has a high reactivity and reacts with the living polymer prior to other functional groups and the Si-Cl bond does not remain at the polymer terminal end. When the living polymer and the silane compound having two or more halogen atoms are reacted, the living polymer tends to conduct coupling and the Si-Cl bond remains at the polymer terminal end, which is not desirable.

The polymer having the Si-Cl bond is extremely instable, easily hydrolyzed with a trace amount of water to evolve noxious gaseous hydrogen chloride in the step of removing the solvent from the polymer solution to form products and in the succeeding storage of products in air. Then, the handling is extremely difficult and, further, it is difficult to control the polymerizing reaction and the crosslinking reaction of the invention.

The silane and siloxane compounds of the invention are preferably reacted by addition of them by one molecule or more, that is, by two or more on the base of the functional groups per one active terminal end of the living polymer. For example, when the difunctional silane or siloxane compound is reacted

by one molecule or less (two or less on the functional base) per one active terminal end, the living polymer conducts coupling to increase the molecular weight and a polymer not containing hydrolysable functional group at the terminal end may intrude.

The reaction between the living polymer and the functional group-containing silane or siloxane compound of the invention is conducted by adding the compound in the solution of the living polymer and, while the reaction temperature can be varied within a wide range, it is preferably from a room temperature to 200°C. Further, while the time required for the reaction depends on the type of the functional group, they are preferably reacted for one min to 20 hours. Generally, the silane or siloxane compound having the Si-Cl bond reacts rapidly and completes reaction substantially instantaneously. On the other hand, reaction between the alkoxy group and like other group, and the living polymer is relatively slow. When the solvent is distilled off after the completion of the reaction, a silane or siloxane-modified polymer containing hydrolysable functional group at the polymer terminal end of the invention is obtained. Alternatively, unreacted silane or siloxane compound may also be removed by distilling off together with the solvent.

The obtained silane-modified polymer can be high-polymerized or crosslinked optionally by

hydrolysis-condensation of the functional groups by bringing it into contact with water under the presence of the silanol condensation catalyst. The degree of high-polymerization and the degree of the crosslinking can be determined depending on the number of active terminal ends of the living polymer and the number of the functional groups of the reacted silane or siloxane compound. For example, the polymer obtained by equi-molar reaction of the living polymer having one active terminal end and the silane compound having two functional groups is a polymer having one functional group in average at one terminal end. Accordingly, in a case of hydrolysis-condensation of the same, a chained polymer having a doubled molecular weight can be obtained. Further, an equi-molar reaction product between the living polymer having two active terminal ends and the difunctional silane compound has one functional group on each of both terminal ends, and a chain polymer of extremely high molecular weight is obtained from the hydrolysis-condensation thereof. Further, when a mixture of a silane-modified polymer having one hydrolysable functional group on one terminal end and a silane-modified polymer having one hydrolysable functional group on each of both end terminals are put to cohydrolysis-condensation, it is also possible to obtain a chained polymer of a desired molecular weight depending on the mixing ratio of them. Further, a polymer obtained by equi-molar reaction of a living

polymer having one active terminal end and a silane compound having three functional groups forms a polymer having two functional groups in average on one terminal. When the polymer is put to hydrolysis-condensation, a comb-type high molecular weight polymer is obtained. Further, when a silane-modified polymer having two functional groups respectively on both terminal ends is put to hydrolysis-condensation, a crosslinked polymer is obtained. Further, a polymer obtained by reacting a living polymer having one active terminal end and a silane compound having four functional groups forms a crosslinked polymer when put to hydrolysis-condensation.

As the silanol condensation catalyst usable in the invention, a wide range of substances have been known to the relevant field of industry and any of such substance can be used in the invention. Such substances includes, for example, carboxylic acid salts such as dibutyl tin dilaurate, stannous acetate, stannous octanoate, lead naphthenate, zinc caprylate, iron 2-ethylhexanoate, and cobalt naphthenate, organic metal compounds such as titanate esters and chelate compounds, for example, tetrabutyl titanate ester, tetranonyl titanate ester, bis(acetylacetonitrile) di-isopropyl titanate, organic bases such as ethylamine, hexylamine, dibutylamine, and pyridine, acids, for example, inorganic acids and aliphatic acids, and alkyl or aryl phosphates.

Preferred catalysts are organic tin compounds, for

example, dibutyl tin dilaurate, dibutyltin diacetate, and dibutyl tin dioctoate.

Under the presence of the silanol condensation catalyst, the silane-modified polymer can be high-polymerized or crosslinked by being in contact with water. In the absence of the catalyst, the silane-modified polymer is stored stably at a room temperature in a tightly closed vessel.

In the presence of the catalyst, the reaction proceeds even with moisture in atmospheric air and, while this is usually sufficient, the crosslinking rate can be increased optionally by the use of atmospheric air in which moisture content is intentionally increased, immersion into liquid water, and use of a properly elevated temperature.

For the high molecular weight or crosslinked polymer obtained by hydrolysis condensation, improvement for various kinds of physical properties is recognized compared with those before the reaction.

The silane-modified polymer of the invention may optionally be mixed with various kinds of thermoplastic resins, for example, low density polyethylene, high density polyethylene, polystyrene, vinyl chloride resin, or ABS resin, and mixed with various kinds of fillers, for example, silane-modified silica, calcium carbonate, dry process silica, wet process silica, glass fibers, calcium carbonate, oil, stabilizer, various kinds of silane and siloxane compounds,

each in an appropriate amount. In this case, the condensative reaction may be conducted before mixing, during mixing, or after mixing them.

From the silane-modified polymer and the composition thereof produced by the method according to the invention, various kinds of practically useful products such as sheets, films, foams, adhesives, shoe soles, injection molding products and various kinds of rubber products can be obtained and, accordingly, it is to be said that the present invention is of a great industrial significance.

Preferred embodiments of the invention are shown below by way of several examples but it should be noted that they describes the gist of the invention more specifically and not restrict the invention.

Example 1

An autoclave of 10 liter inner volume equipped with a stirrer and a jacket is dried and put to nitrogen substitution. While keeping the autoclave at 50°C, previously purified and dried 267 g of styrene and 1.067 g of cyclohexane were supplied, and then a hexane solution of butyl lithium was supplied by 0.75 g as butyl lithium to start polymerizing reaction. One hour after the addition of the catalyst, previously purified and dried 120 g of butadiene, 267 g of styrene, and 1.466 g of cyclohexane were added and the temperature was elevated to

70°C to continue the polymerization. Further one hour after, previously purified and dried 80 g of butadiene, 267 g of styrene, and 1.467 g of cyclohexane were added and polymerized at 70°C for one hour. After the completion of the polymerizing reaction, a red living polymer solution of a styrene-butadiene/styrene-butadiene type block copolymer was obtained.

A portion of the solution was taken and, after adding 2,6-di-tertiary-butyl phenol (BHT) by 1 g per 100 g of the polymer, they were dried to prepare a comparative specimen A.

Further, the solution was left by 2.5 kg in the autoclave (polymer amount: 500 g), and a cyclohexane solution of methyltriethoxy silane (0.5% solution: 220 g) was added thereto at a room temperature and reacted under sufficient stirring for 1 hr. The red color of the polymer solution disappeared and a colorless polymer was obtained. After adding BHT by 1 g per 100 g of the polymer, the solvent and the unreacted silane was distilled off under a reduced pressure and the polymer was dried to obtain a specimen 1. Table 1 shows the result of measuring the number average molecular weight of the specimen 1 and the comparative specimen A by GPC. As apparent from the table, molecular weight of both of them was scarcely changed and it can be seen that the coupling reaction did not occur. Further, when the specimen 1 was formed into a film and when infrared absorption spectrum was measured, an intense

absorption attributable to the Si-O-C bond not present in the polymer before reacting silane was observed near 1100 cm^{-1} .

After mixing one part by weight of dibutyl tin dilaurate to 100 parts by weight of the silane-modified polymer (specimen 1) by shaking, a sheet was prepared by compression molding, which was exposed to steams at 50°C for 20 min to further conduct hydrolysis-condensating reaction. Table 1 shows physical properties of the sheet after the reaction. Physical properties of the compression molded sheet of Comparative Specimen A are also set forth for comparison in Table 1.

As can be seen from Table 1, Specimen 1 of the invention was improved after reaction for the tensile strength and the rigidity (maximum bending stress, bending modulus of elasticity) and, in addition, the transparency was not lowered. Further, it is apparent that the specimen was not dissolved in toluene and increased to such a high molecular weight that the molecular weight could not be measured.

Table 1

Measurement Item	Unit	Specimen 1 for Example	Comparative Specimen A
Styrene content	%	79.5	79.5
Number average molecular weight		91,000	89,000
Tensile strength ¹⁾	kgf/cm ²	407*	300
Elongation ¹⁾	%	85*	80
Tensile modulus of elasticity ¹⁾	kgf/cm ²	11,000*	11,000
Maximum bending stress ²⁾	"	650*	420
Bending modulus of elasticity ²⁾	"	23,000*	16,000
Izot impact value ³⁾	kgf-cm/cm	3.9*	2.1
Rockwell hardness ⁴⁾	R-scale	105*	93
Haze vale ⁵⁾	%	1.5*	1.3
Toluene solubility		Not dissolved (toluene insoluble matter: 100%)	Dissolved

* physical property after hydrolysis-condensation,

1) JIS K 6871,

2) ASTM D 790,

3) JIS K7110,

4) JIS K7202,

5) JIS K6714

Example 2

200 g of styrene and 4 kg of cyclohexane were charged in a nitrogen-substituted autoclave of 10 liter volume, the temperature in the autoclave was kept at 80°C, and 1 g of n-butyl lithium was added being diluted by 10 times with cyclohexane and stirred. After polymerization for 3 hours, 400 g of 1,3-butadiene and 200 g of styrene were charged in the autoclave

and further polymerized for 3 hours at an identical temperature. After polymerization for 3 hours, 200 g of 1,3-butadiene was further added and when polymerized further for 3 hours at an identical temperature, a yellow living polymer solution was obtained. 2.5 kg of the solution was taken out in a tightly closed system to an other nitrogen-substituted autoclave and deactivated by addition of methanol, a stabilizer BHT was added by 0.5 parts by weight based on 100 parts by weight of the polymer. The polymer solution was distilled under a reduced pressure and the solvent was removed to obtain a dry polymer. This is defined as Comparative Specimen B.

50 ml of a cyclohexane solution containing 1.6 g of triethoxychlorosilane was added to 2.5 kg of the active living polymer solution (polymer: 500 g) remained in the autoclave, and stirred sufficiently and reacted at 60°C. 30 min after, the yellow color of the living polymer disappeared to obtain a colorless transparent polymer solution. After adding 1 g of BHT per 100 g of the polymer to the solution, the solvent was distilled under a reduced pressure and, further, unreacted silane was removed by evacuation to obtain a dry polymer (Specimen 2). When the Specimen 2 was formed into a film and the infrared absorption spectrum was measured, an intense absorption attributable to the Si-O-C bond was observed near 1100 cm^{-1} .

Dibutyl tin laurate was added by 1 g per 100 g of the

specimen, mixed in a Brabender, then, a compression molding sheet was prepared, and physical properties were measured after leaving at a room temperature for 20 days. The result is shown in Table 2. For comparison, physical properties of the compression molding sheet of the Specimen B are shown. As apparent from Table 2, crosslinking proceeded in the Specimen 2 while leaving in air and the specimen was made insoluble in toluene and also improved in the oil resistance. Further, it can be seen that permanent elongation at break and compression permanent strain was decreased and improved.

Table 2

Measurement Item method	Measuring	Specimen 2	Comp. Specimen B
Styrene content		40.3	40.3
Hardness	JIS K6301	80	80
300% Modulus	(kg/cm ²) "	23	23
Tensile strength	(kg/cm ²) "	125	120
Elongation	(%) "	900	1200
Elongation at break	(%) "	23	45
Compression permanent strain ¹⁾	(%) "	20	60
Oil resistance ²⁾	"	10	50
Toluene solubility	5% solution stirred at room temperature for 1 hr	Not dissolved	Dissolved in uniform solution

1) Room temperature

2) Swelling test at room temperature for 22 hours according to JIS No. 3 oil